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19 REPUBLIC OF FRANCE

NATIONAL INSTITUTE OF INDUSTRIAL PROPERTY

PARIS 11 Publication No.:

(only to be used for reproduction orders)

21 National Registration No.:

51 Int. Cl.5:

A 61 K 7/00, 9/107 2 700 952

93 00990

12

PATENT APPLICATION

A1

22 Application date: January 29, 1993

30 Priority:

43 Date of public disclosure of the application: June 5, 1994 Bulletin 94/31.

56 List of documents cited in the preliminary research report: Refer to the end of this booklet

60 References to other national documents which appear:

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54 **New cosmetic or dermopharmaceutical compositions in the form of aqueous gels modified by the addition of expanded microspheres.**

57 By adding hollow, expanded microspheres made of thermoplastic material to aqueous gels, cosmetic compositions or base materials for the cosmetic compositions are obtained which have the noteworthy properties of creaminess and smoothness during application, as well as compositions being free from fat. You can thus prepare, for example, compositions of make-up base, of face and body care products, of sun gels, of eye-shadows or skin-cleansing products, included in the form of facial masks.

The purpose of the invention is new cosmetic or dermatopharmaceutical compositions in the form of aqueous gels modified by the addition of expanded microspheres.

It is known that in the preparation of cosmetic or dermatopharmaceutical compositions, compositions in the form of emulsions, such as creams, are often used. The emulsions, which can be of the water-in-oil type or oil-in-water type, are made up of two non-miscible and surface-active phases having the role of stabilizing the dispersion of one of the phases, or dispersed phase, into the continuous phase.

Emulsions of this type are usually creamy. However, as a function of the quantity and the quality of the oil used, the user can feel an effect which is more or less unpleasant, and see a sticking effect. In addition, the emulsifying agent, the presence of which is necessary in order to stabilize the emulsion, can prove to be more or less irritating for the skin.

In addition, some cosmetic or dermatopharmaceutical compositions are presented in the form of aqueous gels. It is known that a gel is in an intermediate state between a solid state and a liquid state.

It is accepted that a gel consists of a three-dimensional network of molecules which holds a sizable quantity of solvent in its meshes. The formation of a network of this type constitutes jellification. Depending on the nature of the solvent, a hydrogel or organogel is obtained.

One of the interests in the use of compositions in the form of hydrogels is that they bring an agreeable feeling of freshness to the application, without the unpleasant effect of greasiness. However, an effect of stickiness and an effect of tension in the skin occurs during an application with a massage or after application, when the water evaporates.

Now, it has been discovered that, in a surprising way, it is possible to obtain compositions which preserve the qualities of the gels without having the disadvantages of them, by the introduction of hollow expanded microspheres into a hydrophilic gel without oil. In spite of the absence of oil, the gels which have been modified in this way have a lasting creaminess during the application, which is particularly easy and agreeable. Even after drying, the skin does not have any stickiness to the touch and the user does not feel any feeling of tension in the skin.

Until now, hollow expanded microspheres had been used in compositions in the form of powders, or in the form of emulsions, or even in order to obtain compositions having the appearance of a lather (mousse); see for example the patents JP-60 184004, FR-2.472.382, FR-2.658.720, FR-2.669.222 or DE-2.521.003. In practice, known cosmetic compositions using the hollow expanded microspheres always contained fat. It was not obvious that the incorporation of these microspheres in the aqueous gels without oil would make it possible to obtain a creaminess when the dispersion had been, until the present time, only obtained with compositions containing fat.

Thus the compositions of the invention bring much comfort and softness to the application. In addition, after application, the skin retains a olive appearance. Also, the compositions of the invention have a viscosity which stays roughly constant when the

temperature is increased (contrary to what one observes currently with the creams) in a manner so that their use stays agreeable even in hot countries or during the hot seasons.

The purpose of the invention is thus a cosmetic or dermopharmaceutical composition, or a base material for the cosmetic or dermopharmaceutical composition, in the form of modified gel, characterized by the fact that it consists of hollow, expanded microspheres dispersed in an aqueous gel, that the aforementioned hollow microspheres are expanded microspheres made of thermoplastic material having a specific mass of 15 to 200 kg/m³, that the aforementioned composition or the aforementioned base material contains from 0.1 to 10% by weight of the aforementioned microspheres relative to the total weight of the composition or base material, and that the aforementioned composition or the aforementioned base material is free of fat.

The expanded microspheres made of thermoplastic material are known and can be obtained, for example, according to the procedures described in the patents and patent applications EP-56219, EP-348572, EP-486080, EP-320473, EP-112807, and US-3.615.972.

These microspheres can be made from any non-toxic and non-irritating thermoplastic material. For example, polymers or copolymers of acrylonitrile or vinylidene chloride could be used. You could use, for example, a copolymer containing, by weight, from 0 to 60 % of units derived from vinylidene chloride, from 20 to 90 % of units derived from acrylonitrile, and from 0 to 50 % of units derived from an acrylic or styrene monomer, the sum of the percentages (by weight) being equal to 100. The acrylic monomer is, for example, methyl or ethyl acrylate or methacrylate. The styrene monomer is for example, alpha-methyl styrene or styrene. The microspheres can be in a dry or hydrated state.

The inside cavity of the hollow, expanded microspheres contains a gas, which can be a hydrocarbon such as isobutane, isopentane, or even air. Among usable hollow microspheres, reference is made in particular to the ones marketed under the trademark Expancel by the Kémanord Plast company, particularly those of the quality DE (dry state) or WE (hydrated state).

In the compositions or base materials for the compositions of the invention, the weight percentage of the hollow, expanded microspheres is preferably between 0.5 and 5 %. The texture of the gels is particularly creamy for the percentages from 0.5 to 2%, generally around 1 to 2%. The texture is more like a paste for the proportions from 2 to 5% which is more particularly suitable for certain skin-cleansing products or for products designed to be applied in a thick layer (masks).

The hollow microspheres generally have average dimensions of the particles which can vary from 5 to 250 μm , and in specific, from 10 to 150 μm .

In order to make the gel which is at the base of the composition or the base material of the invention, you use at least one jellifying agent in an aqueous liquid medium. Of course, the jellifying agent is present in a sufficient quantity to give the composition the desired viscosity, which is a function of the intended use, of course. This viscosity can run, for example, from 3 to 200 poise (or 0.3 to 20 Pa.s).

For example, if it is desirable to obtain creamy products, the viscosity is adjusted to a value of between 10 and 50 poise (or between 1 and 5 Pa.s). If it is desirable to make the products more viscous, in particular usable as masks, the viscosity is adjusted, for

example, to a value between 20 and 200 poise, and in particular, between 20 and 100 poise. For compositions used as scrubs for the skin, the viscosity is between, in particular, approximately 10 and 100 poise (or between 1 and 10 Pa.s).

The jellifying agents are selected particularly from among the hydrosoluble polymers or those giving colloidal solutions in water.

These are, in particular, polymers or copolymers of unsaturated carboxylic organic acids or unsaturated esters, derivatives of polysaccharides, gums, colloidal silicates, polyethylene glycols (PEG) and their derivatives, polyvinyl pyrrolidones and their derivatives, and gels of hydrophilic silica.

The jellifying agents are, for example, acrylic and/or methacrylic polymers or copolymers, carboxyvinyl polymers, acrylates or methacrylates of polyglyceryls, derivatives of cellulose or starch, derivatives of chitin, alginates, hyaluronic acid and its salts, chondroitin sulfates, gums of xanthane, gellane, Rhamsan, karoya or guar, carob flour, and colloidal silicates of aluminum and magnesium of the montmorillonite type.

Cited, in particular, as specific jellifying agents can be: carboxyvinyl polymers sold under the name Carbopol (Goodrich), acrylic acid/ ethyl acrylate copolymers, acrylic acid/ methacrylate of stearyl copolymers, polyglyceryl methacrylate sold under the name Lubrajel (Guardian), polyglyceryl acrylate sold under the name Hispagel (Hispano Chimica), carboxymethyl cellulose, hydroxymethyl cellulose, hydroxypropyl cellulose, microcrystalline cellulose, hydroxypropyl guar, colloidal hectorites or bentonites sold under the name Veegum, etc...

The compositions of the invention can also contain the various ingredients used in the cosmetic or dermatopharmaceutical compositions, notably the pigments, coloring agents, preservatives, hydrating agents, perfumes, texture agents, such as the pulverulent agents other than the hollow microspheres, agents absorbing ultraviolet, etc...

The pigments can be mineral pigments, organic pigments or pearly pigments. Among the mineral pigments could be cited, for example, titanium (IV) oxide, black, yellow, red or brown iron oxides, manganese violet, ultramarine violet, ultramarine blue, chromium (III) oxide, etc...

Among the organic pigments could be cited in particular the pigments D & C Red No. 3, No. 6, No. 7, No. 9, No. 13, No. 19, No. 21, No. 27, No. 30, or No. 36, or even carbon black.

The pearly pigments can be selected from among pearly white pigments, such as mica covered with titanium (IV) oxide or with bismuth oxychloride. You can also use colored pearly pigments, such as titanium mica colored with iron oxides or with chromium (III) oxide, titanium mica colored with an organic pigment of the aforementioned type, or even pearly pigments based on bismuth oxychloride.

As coloring agents, you can use hydrosoluble coloring agents such as ponceau disodic salt, alizarin green disodic salt, chinoleine yellow, trisodium salt of amaranth, disodium salt of tartrazine, monosodium salt of rhodamine, disodium salt of aniline red, xanthophyll, etc...

Among those usable ingredients which are soluble in water, are mentioned, in particular, the polyalcohols such as propylene glycol, butylene-1,3 glycol, glycerine, polyglycerine, D-sorbitol, glucose, sucrose, magnesium gluconate, trace elements, silicone acids soluble in water, etc...

Some compositions of the invention (particularly the make-up or cleansing products) can likewise contain pulverulent materials, particularly clay of the montmorillonite type, hectorite or bentonite for cleansing products or other materials such as silicas or silicone powders (Tospearl) or polyamides (nylon) or the polymethacrylate powder of methyl (Micropearl) in order to obtain optical effects.

To prepare the compositions of the invention, you dissolve the soluble ingredients in the aqueous liquid medium, then you add the jellifying agent(s). You then introduce the hollow, expanded microspheres. The materials can be added before or after the introduction of the jellifying agent. The procedure requires neither a violent agitation nor an addition of heat if all the components are soluble at room temperature. You will then be able to use, without problems, the gels sensitive to shearing and ingredients sensitive to temperature.

Among the compositions (or base materials) of the invention, those having the good qualities of creaminess are, in particular, the ones which contain from 0.1 to 2 %, and in particular, from 0.5 to 1% of hollow, expanded microspheres by weight relative to the total weight of the composition, the aforementioned micros [sic] amines, keratin derivatives, vitamins, antioxidants, the pheres [sic] having dimensions of 5-50 μm and in particular, 10-30 μm . These compositions consist, in particular, in the form of creamy gels, of face and body care products, of sun gels, of after-shave products, of make-up products of the make-up base type, blush or eye-shadow, or make-up removal products.

The compositions consisting of a skin cleansing product in the form of a facial mask contain, for example, from 2 to 5 % by weight of hollow microspheres having dimensions from 10 to 50 μm .

The compositions of scrubs for the skin contain, for example, from 0.5 to 5 % by weight of hollow microspheres. The aforementioned microspheres have average dimensions of from 80 to 250 μm , and in particular, 100 to 250 μm .

The invention also has as a purpose, the use of hollow microspheres, such as those previously defined, as additives designed to improve the ease and softness of the application of a cosmetic or dermatopharmaceutical aqueous gel which is free from fat.

The invention also has as a purpose, a cosmetic treatment process characterized by the fact that one applies to the skin a cosmetic composition such as the one previously defined.

The following examples illustrate the invention.

In these examples, the percentages are by weight.

EXAMPLE 1: SKIN GEL

- Expancel EL 23 (KEMANORD).....	1%
- Carbopol 954.Goodrich (Carbomer).....	1.5%
- Polyvinylpyrrolidone.....	1%
- Polyethylene glycol.....	8.4%
- Tri-ethanol amine.....	2.5%
- Preservative.....	0.5%
- Water.....	qsp 100%

This gel is prepared in the following manner: to the water which contains the preservative, add progressively under agitation: the Carbopol, the polyvinyl pyrrolidone, and the polyethylene glycol; neutralize this by the tri-ethanol amine, then introduce the Expancel at room temperature.

Result: A very soft, creamy care gel is obtained which is not greasy and not sticky.

Characteristics of the Expancel EL 23:

- average granulometry : 18 μm
- density : 69.4 kg/m^3
- internal gas : isobutane

EXAMPLE 2: BLUSH

In a similar manner, a gel having the following composition is prepared:

- Expancel EL 23 (KEMANORD)..... 1%
- Carbopol 954 Goodrich (Carbomer)..... 1.50%
- Polyvinylpyrrolidone..... 1%
- Polyethylene glycol..... 8.40%
- Tri-ethanol amine..... 2.50%
- Preservative..... 0.50%
- Red coloring agent soluble in water
(disodium salt of ponceau)..... 0.18%
- Black coloring agent soluble in water
(disodium salt of alizarin green)..... 0.22%
- Water..... qsp 100%

Results: A blush is obtained in the form of a creamy gel having a reddish pink color, easy to apply, soft. The make-up obtained is very natural and clear.

EXAMPLE 3: MAKE-UP BASE

- Expancel EL 23 (KEMANORD)..... 1%
- Carbopol 954 Goodrich (Carbomer)..... 1.488%
- Polyvinylpyrrolidone..... 0.99%
- Polyethylene glycol..... 8.40%
- Tri-ethanol amine..... 2.475%
- Glycerine..... 2%
- Preservative..... 0.30%
- Yellow coloring agent soluble in water
(chinoleine yellow)..... 0.07%
- Red coloring agent soluble in water
(disodium salt of ponceau)..... 0.09%

- Black coloring agent soluble in water
(disodium salt of alizarin green)..... 0.04%
- Water..... qsp 100%

Result: A make-up base is obtained in the form of a gel having a caramel color which spreads easily and is completely fat-free, but stays creamy and soft, however. The make-up is very natural and of good quality.

EXAMPLE 4: SCRUB (cleansing product)

- Expancel EL 16 (KEMANORD)..... 1%
- Carbopol 954 Goodrich (Carbomer)..... 2%
- Tri-ethanol amine..... 2.50%
- Preservative..... 0.50%
- Glycerine..... 3%
- Water..... qsp 100%

Result: A soft scrub for the skin is obtained. It is applied by massaging the skin and then removing the remaining formation by rinsing with water. The skin will stay very soft.

Characteristics of the Expancel EL 16:

- average granulometry : 90 μm
- density : 28.8 kg/m^3
- internal gas : isopentane

EXAMPLE 5: SKIN CLEANSING GEL

- Expancel EL 3 (KEMANORD)..... 1.5%
- Carbopol 954 GOODRICH (Carbomer)..... 0.95%
- Tri-ethanol amine..... 1%
- Butylene glycol..... 5%
- Carrageenan..... 0.50%
- Dodecanediol polyglycerol*..... 2.50%
- Preservative..... 3%
- Water..... qsp 100%

* Dodecanediol polyglycerol : product obtained by grafting 3 moles of glycerol onto dodecanediol ; see FR.2.091.516.

Result: A cleansing gel is obtained which is very soft and contains large-sized microspherules, visible to the naked eye, having a massaging and cleansing action during application. It is rinsed with water as is done with soap.

Characteristics of the Expancel EL 3:

- average granulometry : 87 μm
- density : 21 kg/m^3
- internal gas : isopentane

EXAMPLE 6: MASK (facial cleansing product)

- Expancel EL 4 (KEMANORD)..... 5%
- Polyvinylpyrrolidone..... 2.50%
- Polyglycerine 500 (SOLVAY)..... 5%
- Preservative..... 3%
- Water..... qsp 100%

Result: A pasty product is obtained which has a creamy appearance and which one spreads on the skin in a thick layer and lets dry for 10 minutes. The product absorbs the fatty substances on the surface of the skin without any feeling of pulling pain. It is removed very easily with water, leaving the skin very soft.

Characteristics of the Expancel EL 4:

- average granulometry : 17 μm
- density : 115 kg/m^3
- internal gas : isobutane

EXAMPLE 7: AQUEOUS SUN GEL

- Hydroxypropyl ether of cellulose* (PM: 300,000)..... 3%
- Acid B-B' camphosulfonic (1-4 divinylbenzene)
in 33% aqueous solution 6.06%
- Tri-ethanol amine at 99%..... 1.2%
- expanded microspheres (Expancel EL 23)..... 0.5%
- Sterilized demineralized water..... qsp 100%

This gel is fresh and soft in application and protects from solar radiation.

* commercial name KLUCEL G (Hercules)

EXAMPLE 8: AFTER SHAVE GEL

- Acrylic acid /methacrylate of stearyl copolymer..... 0.05%
- Polyethylene glycol 800..... 2.50%
- Glycerine..... 1.50%

- Ethanol.....	38%
- Allantoin.....	0.05%
- Menthol.....	0.02%
- Tri-ethanol amine.....	0.75%
- Preservative.....	0.01%
- Expancel EL 23 (KEMANORD).....	0.75%
- Water.....	qsp 100%

This gel is fresh, soft and soothing.

The following comparative examples show that the interesting results, which are obtained by the addition of hollow expanded microspheres to the aqueous gels, are not obtained with other microspheres.

COMPARATIVE EXAMPLE No. 1

Gel containing microspherules of silicone resin

This gel has the following composition (% weight):

- Silicone spheres : TOSPEARL 108* (TOSHIBA).....	5%
- Carbopol 954 GOODRICH (Carbomer).....	1.5%
- Polyvinyl pyrrolidone.....	1%
- Polyethylene glycol.....	8.40%
- Tri-ethanol amine.....	2.50%
- Preservative.....	0.30%
- Water.....	81.30%

*TOSPEARL 108 (trademark) : this material, of very fine granulometry, is well-known for adding softness in the sector of aqueous cosmetics.

Result: At application, one notices a rapid reduction in the ease of dispersion and a sticky and dry effect. The product ends by becoming fluffy when the massage is continued.

Comment: If you prepare a similar formula having 10% Tospearl 108, you will obtain an identical result.

COMPARATIVE EXAMPLE No. 2

Gel containing microporous spheres of methyl polymethacrylate

- Spheres of Micropearl M* (MATSUMOTO).....	5%
- Carbopol 954 (GOODRICH)	1.5%
- Polyvinyl pyrrolidone.....	1%
- Polyethylene glycol.....	8.40%
- Tri-ethanol amine.....	2.50%
- Preservative.....	0.30%
- Water.....	81.30%

* Micropearl M : ultra-fine microporous spherical powder having open cavities, developed especially for cosmetic applications, having a very soft touch to the skin ; size = 10 μm .

Result: - gel having a good appearance
 - sticky at application,
 - very dry effect,
 - fluffy.

Comment: You obtain the same result using 10% of Micropearl M.

COMPARATIVE EXAMPLE No. 3

Gel containing microspherules of silica having a cavity SB - 700 - Silica beads

- SB 700*.....	5%
- Carbopol 954 GOODRICH (Carbomer).....	1.5%
- Polyvinyl pyrrolidone.....	1%
- Polyethylene glycol.....	8.40%
- Tri-ethanol amine.....	2.50%
- Preservative.....	0.30%
- Water.....	81.30%

* SB 700 : microporous, hydrophilic powder of mineral origin having a size from 1 to 17 μm (MAPRECOS).

Result: During and after application, the touch of it to the skin is not pleasant.

These comparative examples show that you can not, even using other hollow microspheres, obtain the cosmetic effects given to aqueous gels by the hollow expanded microspheres of thermoplastic material, which have the particularity of adding a good deal of softness in application, and comfort.

CLAIMS

1. Cosmetic or dermopharmaceutical composition, or a base material for the cosmetic or dermopharmaceutical composition, in the form of a modified gel, characterized by the fact that it consists of hollow, expanded microspheres dispersed in an aqueous gel, that the aforementioned hollow microspheres are expanded microspheres made of thermoplastic material having a specific mass of 15 to 200 kg/m³, that the aforementioned composition or the aforementioned base material contains from 0.1 to 10% by weight of the aforementioned microspheres relative to the total weight of the composition or base material, and that the aforementioned composition or the aforementioned base material is free of fat.

2. Composition or base material according to claim 1, characterized by the fact that the aforementioned hollow microspheres have average dimensions of the particles which can vary from 5 to 250 μ m, and in specific, from 10 to 150 μ m.

3. Composition or base material according to one of the previous claims, characterized by the fact that the aforementioned gel consists of at least one jellifying agent in an aqueous liquid carrier, the aforementioned jellifying agent is selected particularly from among hydrosoluble polymers or those giving colloidal solutions in water.

4. Composition or base material according to the preceding claim, characterized by the fact that the aforementioned jellifying agent is selected from among polymers or copolymers of unsaturated carboxylic organic acids or unsaturated esters, derivatives of polysaccharide, gums, colloidal silicates, polyethylene glycols (PEG) and their derivatives, polyvinyl pyrrolidones and their derivatives, and gels of hydrophilic silica.

5. Composition or base material according to claim 3 or 4, characterized by the fact that the aforementioned jellifying agent is selected from among acrylic and/or methacrylic polymers or copolymers, carboxyvinyl polymers, acrylates or methacrylates of polyglyceryls, derivatives of cellulose or starch, derivatives of chitin, alginates, hyaluronic acid and its salts, chondroitin sulfates, gums of xanthane, gellane, Rhamsan, karoya or guar, carob flour, and colloidal silicates of aluminum and magnesium of the montmorillonite type.

6. Composition or base material according to one of the previous claims 3 to 5, characterized by the fact that the aforementioned jellifying agent is present in a quantity sufficient to give the aforementioned composition the viscosity desired for the aforementioned composition or aforementioned base material.

7. Composition or base material according to the preceding claim, characterized by the fact that the aforementioned viscosity can go, for example, from 3 to 200 poise (or 0.3 to 20 Pa.s).

8. Composition or base material according to one of the previous claims, in the form of a creamy gel, characterized by the fact that it contains the hollow, expanded microspheres at the ratio of 0.1 to 2% by weight relative to the total weight of the composition, and that the aforementioned microspheres have dimensions from 5 to 50 μ m, and in specific, from 10 to 30 μ m.

9. Composition or base material according to one of the previous claims, characterized by the fact that it consists of a face or body care product, a sun gel, an after-shave product, a make-up product of the make-up base type, blush or eye-shadow, or a make-up removal product.

10. Cosmetic composition according to one of the claims 1 to 7, characterized by the fact that it contains from 2 to 5 % by weight of aforementioned microspheres relative to the total weight, the aforementioned microspheres having dimensions from 10 to 50 μm , the aforementioned composition constituting a skin cleansing product in the form of a facial mask.

11. Cosmetic composition according to one of the claims 1 to 7, characterized by the fact that it contains from 0.5 to 5 % by weight of hollow microspheres and that the aforementioned microspheres have average dimensions of from 80 to 250 μm , and in particular, 100 to 250 μm , and the aforementioned composition is a skin cleansing product in the form of a scrub for the skin.

12. Use of hollow microspheres such as the ones defined in one of the claims 1, 2, 8, 10, and 11, as additives designed to improve the ease and the softness of the application of a cosmetic or dermopharmaceutical aqueous gel free from fat.

13. Process for cosmetic treatment, characterized by the fact that one applies to the skin a cosmetic composition such as that defined in one of the claims 1 to 11.

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Investigation Report

performed on the basis of the latest claims submitted before the start of the investigation

2 700 952

National registration number

FA 481122

FA 9300990

Relevant Documents

Category involved	Document reference with statement, if necessary, of the significant parts	Claims
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EP-A-0 486 394 (L'OREAL)

* the entire document *

& FR-A-2 669 222

GB-A-2 238 242 (MAYBE HOLDING CO)

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DE-A-15 69 467 (NATIONAL HOME PRODUCTS INC)

* the entire document *

1-13

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Investigated technical areas (Int. Cl.5)

A61K

Concluding date of the investigation

Investigator

October 29, 1993

FISCHER, J.

Categories of the documents cited

X: of special meaning when observed alone

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